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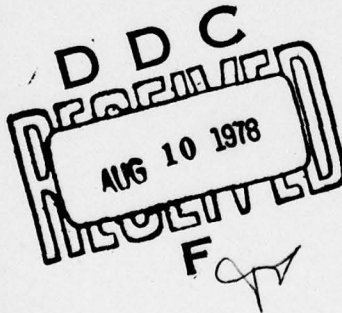
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FJSRL TECHNICAL REPORT-78-0001

MAY 1978

STUDIES OF $O_2(^1\Delta_G)$ PRODUCTION

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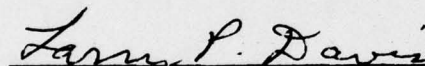UNITED STATES AIR FORCE

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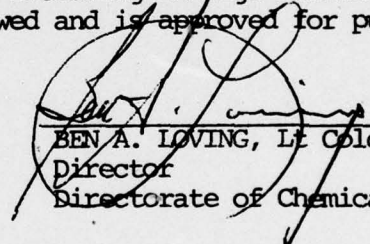
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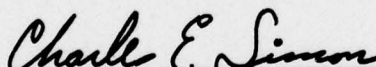
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Production and deactivation of singlet delta oxygen has been measured with electron spin resonance spectroscopy. Microwave discharge and chemical reactions were used to produce the excited oxygen. Deactivation rate measurements of the excited oxygen by self- and wall collisions as well as with gaseous chlorine have been accomplished. Results indicate insignificant deactivation by chlorine.

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STUDIES OF $O_2(^1\Delta_g)$ PRODUCTION

AND DEACTIVATION

By

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Maj Chester J. Dymek

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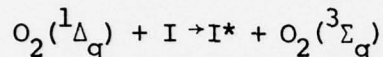   SPECIAL

i

TABLE OF CONTENTS

LIST OF FIGURES

iii

I. Introduction

One of the more promising electronic transition laser systems is the $O_2(^1\Delta_g)/I$ chemical laser. The basis for this potential new laser system is energy transfer from $O_2(^1\Delta_g)$ to I:

$$O_2(^1\Delta_g) + I \rightarrow I^* + O_2(^3\Sigma_g)$$

followed by lasing on I^*. One of the key requirements for successful lasing is a substantial ratio of $O_2(^1\Delta_g)$ to ground state oxygen $O_2(^3\Sigma_g)$.

Two potential methods for producing suitable concentrations of $O_2(^1\Delta_g)$ are via microwave discharge of O_2 and via chemical reactions. Microwave discharge of O_2 has been thoroughly investigated at AFWL and here at the USAF Academy[1], and it appears the maximum percentage of $O_2(^1\Delta_g)$ that can be produced is about 15%, considerably short of what is required for successful lasing. Chemical generators have been employed both at FJSRL under previous work units[2,3] and at various AFWL contractor's installations[4] to attain promising yields of $O_2(^1\Delta_g)$. Attempts to observe lasing with systems utilizing chemical generators are currently underway at AFWL. The first demonstration of this laser was recently reported by AFWL personnel as having occurred on 1 December 1977 at their facility[5].

The chemical generator systems which have been successful to date have employed reaction of halogens or halogen-containing compounds with basic hydrogen peroxide solutions to produce the $O_2(^1\Delta_g)$. The initial goal for this work unit was to chemically engineer a Cl_2/H_2O_2 generator developed under a previous work unit[2,3] to optimize the production of $O_2(^1\Delta_g)$. Due to success of other chemical generator systems, this goal was abandoned in favor of other objectives. These included studies of

1

self-deactivation of $O_2(^1\Delta_g)$, deactivation of $O_2(^1\Delta_g)$ and I^* by Cl_2, and determination of HCl content of the exhaust from the Cl_2/H_2O_2 chemical generator system. This report documents progress to date on these three goals.

Self-deactivation of $O_2(^1\Delta_g)$ was studied by measuring $O_2(^1\Delta_g)$ concentrations at various distances downstream from the production point. The excited O_2 was produced via microwave generation and both $O_2(^1\Delta_g)$ and $O_2(^3\Sigma_g)$ were measured with ESR. The results of this study provided a rough estimate of how much $O_2(^1\Delta_g)$ was lost via self- and wall deactivation for various downstream distances. No attempt was made to separate the two effects.

Preliminary estimates of the deactivation of Cl_2 on $O_2(^1\Delta_g)$ were made by comparison with Ar deactivation. More reliable equipment is on order to establish a quantitative result for the deactivation rate.

Attempts to measure HCl in the exhaust of a Cl_2/H_2O_2 generator with mass spectrometry and IR spectrometry have been made. Problems have arisen with both methods, but work is continuing.

II. Experimental

Self-Deactivation of $O_2(^1\Delta_g)$

The $O_2(^1\Delta_g)$ was produced via microwave discharge. Nominal operating conditions for the microwave unit were seventy watts total power with less than two watts reflected power. Flow rates were varied from about 15 STDCC/min to 85 STDCC/min and pressures from about .5 to 2 torr. Flow rate was measured with a Matheson thermal conductivity type flow-meter and pressures with a Baratron capacitance-type pressure gauge with a 10 torr head.

$O_2(^1\Delta_g)$ and $O_2(^3\Sigma_g)$ concentrations were measured via ESR. A Varian 4502 spectrometer utilizing 100 Kc modulation monitored the $K=3$, $J=4$, $M=3 \rightarrow 4$ transition of $O_2(^3\Sigma_g)^6$ (the so-called "A-line") and one of the center quadruplets of the $O_2(^1\Delta_g)$ spectrum. Using these lines, the ratio of the concentration can be given in terms of the ratio of the intensities by

$$(1) \quad \frac{C(^1\Delta_g)}{C(^3\Sigma_g)} = .624 \times \frac{I(^1\Delta_g)}{I(^3\Sigma_g)}$$

in which

$$C(^1\Delta_g) = \text{concentration of } O_2(^1\Delta_g)$$

$$C(^3\Sigma_g) = \text{concentration of } O_2(^3\Sigma_g)$$

$$I(^1\Delta_g) = \text{intensity of } O_2(^1\Delta_g) \text{ ESR peak}$$

$$I(^3\Sigma_g) = \text{intensity of } O_2(^3\Sigma_g) \text{ ESR peak}$$

The factor of .624 relates the theoretical intensities of the two lines measured. The intensities were estimated from the ESR peaks by taking

3

the peak-to-peak height of the derivative spectrum and multiplying by the square of the peak-to-peak width ($H \times W^2$). This approximation saves considerable effort in replacing the double integration which would have to be done in order to get the area under the absorption curve otherwise and is estimated to be accurate to within a few percent. The fraction of $O_2(^1\Delta_g)$ of the total O_2 can be obtained from the concentration ratio.

$$(2) \quad f(^1\Delta_g) = \frac{C(^1\Delta_g)}{C(^3\Sigma_g)} \left(1 + \frac{C(^1\Delta_g)}{C(^3\Sigma_g)} \right)^{-1}$$

in which $f(^1\Delta_g)$ is the fraction of the total O_2 flow which is $O_2(^1\Delta_g)$.

Oxygen atoms were also detected in the flow via ESR. There is a strong oxygen atom line near 3500 G which was used to detect the O atoms.

The distance between the microwave production of $O_2(^1\Delta_g)$ and the ESR measurements was varied between 80 and 211 cm under the variety of flow rate and pressure conditions mentioned previously. A schematic of the experimental apparatus is shown in Figure 1. The glass and tygon tubing between the microwave and ESR was 3/8" I.D.

Deactivation of $O_2(^1\Delta_g)$ by Cl_2

Production of the $O_2(^1\Delta_g)$ was accomplished with the microwave discharge unit as described in the previous section. Measurement of $O_2(^1\Delta_g)$ and $O_2(^3\Sigma_g)$ was made with the ESR, also as described in the previous section. Varying amounts of Cl_2 or Ar were introduced into the O_2 flow downstream of the $O_2(^1\Delta_g)$ production. Argon was used to insure
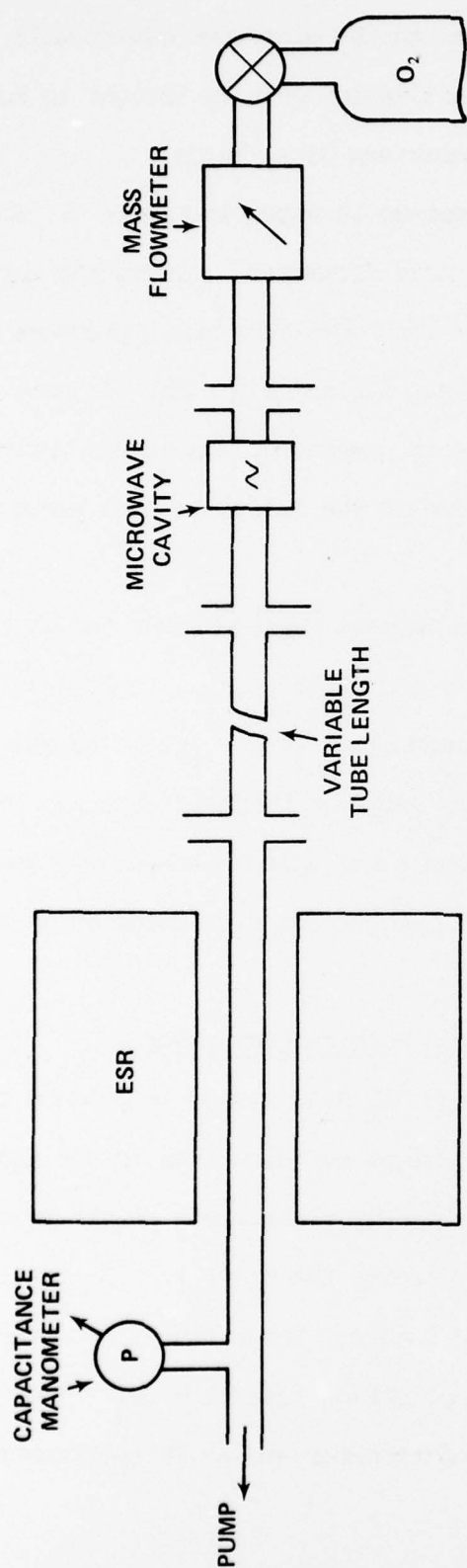
FIGURE 1. EXPERIMENTAL SET-UP FOR SELF-DEACTIVATION OF $O_2(^1\Delta_g)$.

the same pressure-flow rate conditions in the microwave cavity with the Cl_2 as without. The $Ar - O_2(^1\Delta_g)$ deactivation rate is thought to be quite small, affording a point of comparison with the Cl_2

A schematic of the experimental set-up is shown in Figure 2. Either Cl_2 or O_2 can be shunted through the mass flowmeter. During the experiments the O_2 pressure was kept near 1 torr while the total pressure $(Ar + O_2$ or $Cl_2 + O_2)$ was varied between 1.3 and 2.0 torr. It must be recognized that because of the different pumping speeds of the various gases the total pressure is not the sum of the individual gas pressures measured by themselves.

The conditions which were matched between the Ar/O_2 and the Cl_2/O_2 experiments were total system pressure and O_2 flow rate. This assured the same $O_2(^1\Delta_g)$ production rate in each case. The O_2 pressure and flow rate were first set with only O_2 being pumped through the system. Then enough Ar or Cl_2 was added to bring the total system pressure up to the desired value. This procedure required different flow rates of Ar or Cl_2 to achieve the desired match.

Determination of HCl Content from a Chemical Generator

The chemical generator utilized the Cl_2/H_2O_2 system to produce the $O_2(^1\Delta_g)$. NaOH in the amount of 12% by weight was dissolved in 90% H_2O_2. About 20 ml of this solution was poured over glass beads in the reactor. Cl_2 was bubbled through the solution forming the $O_2(^1\Delta_g)$. The total system pressure was maintained around 2 torr. The effluent from the reaction was frozen out in a sample collection tube with LN_2. The sample was then analyzed on a mass spectrometer and an IR spectrometer

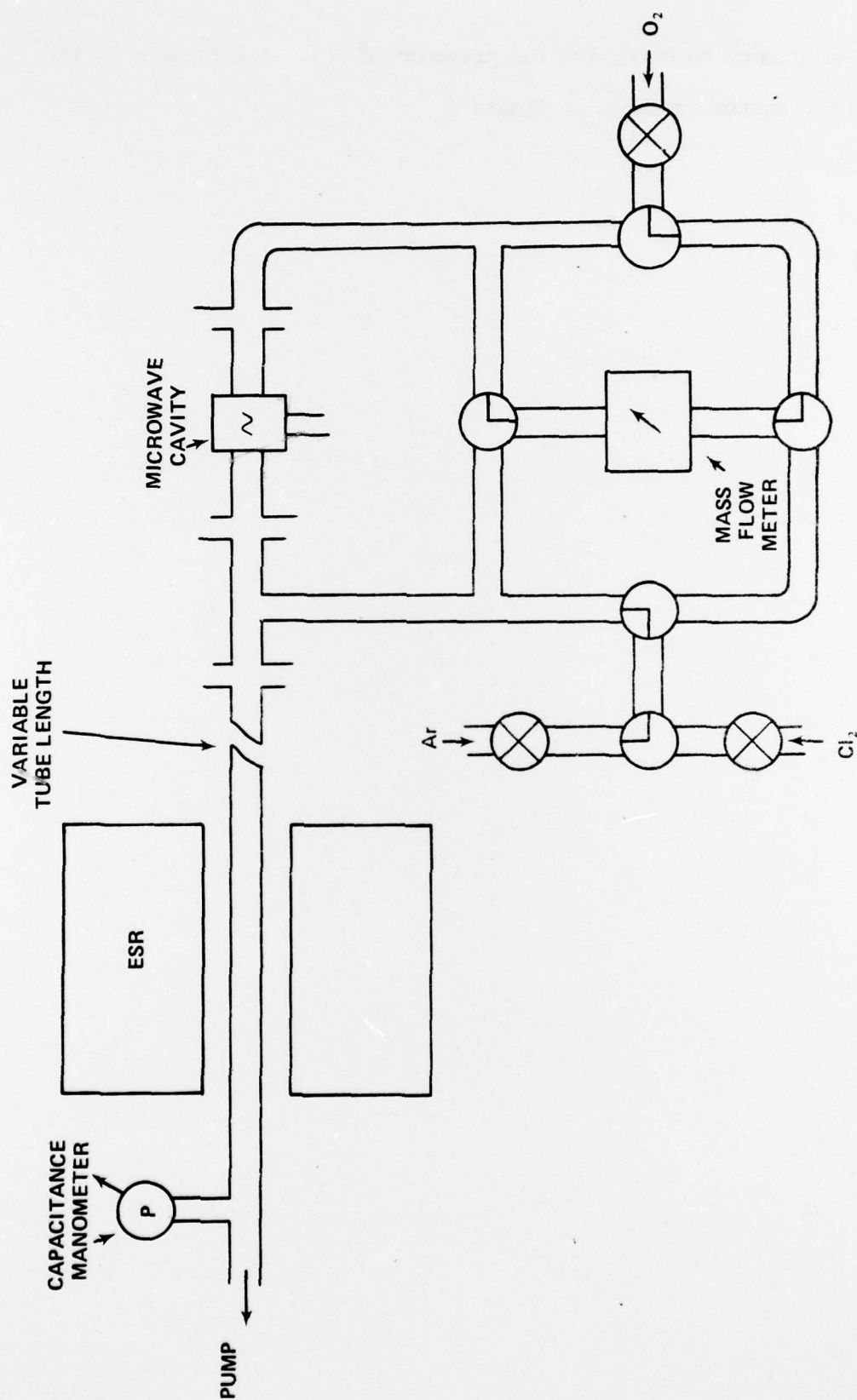6

FIGURE 2. EXPERIMENTAL SET-UP FOR Cl_2 DEACTIVATION OF $O_2(^1\Delta_g)$

in an attempt to determine the presence of HCl. A schematic of the
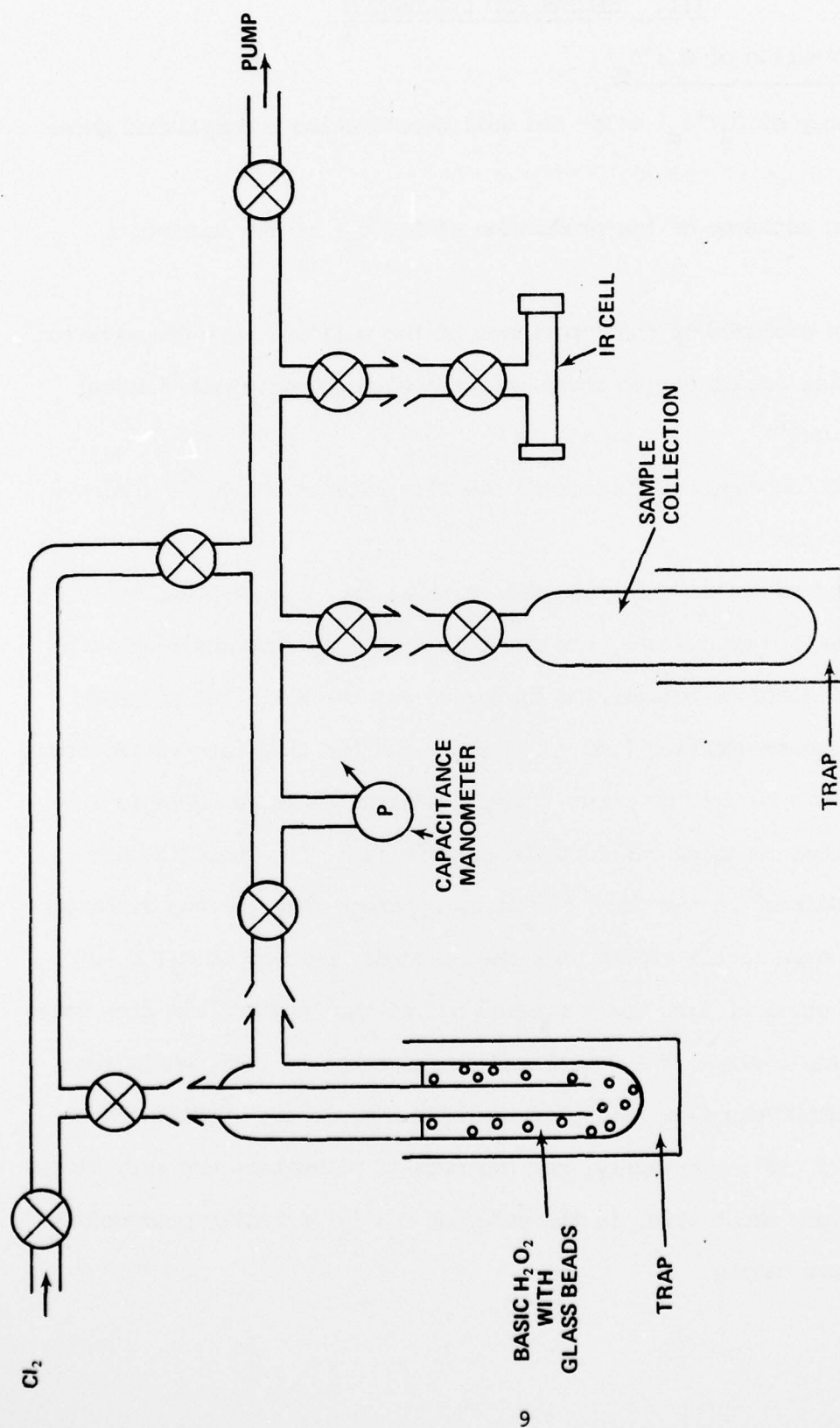reactor system is shown in Figure 3.

FIGURE 3. EXPERIMENTAL SET-UP FOR DETECTION OF HCl AS A PRODUCT FROM THE Cl_2/H_2O_2 REACTION.

PUMP

IR CELL

SAMPLE COLLECTION

TRAP

CAPACITANCE MANOMETER

P

BASIC H_2O_2 WITH GLASS BEADS

TRAP

Cl_2

9

III. RESULTS AND DISCUSSION

Self-Deactivation of $O_2(^1\Delta_g)$

The study of $O_2(^1\Delta_g)$ self- and wall deactivation accomplished three goals:

(1) An estimate of the production of $O_2(^1\Delta_g)$ at the microwave cavity.

(2) An estimate of the importance of the wall and self-deactivation under similar conditions to those utilized with the previous chemical generator work[2,3].

(3) The dependence of pressure and flow rate on the $O_2(^1\Delta_g)$ microwave production.

In order to obtain the production rate at the microwave and the self- and wall deactivation, the fraction of $O_2(^1\Delta_g)$ was measured as a fraction of distance between the microwave and the ESR. The pressure for all of these data was $1.00 \pm .05$ torr, and the flow rate varied from 15.5 STDCC/min to 51 STDCC/min. These data are tabulated in Table 1. Figure 4 shows in graphical form the data in Table 1. There is considerable scatter in the data, but it is apparent that the two different flow rates have little effect upon the measured fraction of $O_2(^1\Delta_g)$. In fact, a straight line least squares bit of the 16 STDCC/min flow rate points yields a slope of -.000212 and an intercept of .125, while that of the 50 STDCC/min flow rate points yields a slope of -.000192 and an intercept of .127. Obviously, the two sets of parameters are very close. The intercept, about .126, is the value of $O_2(^1\Delta_g)$ actually produced at the microwave cavity.

10

TABLE I

Fraction of $O_2(^1\Delta_g)$ at One Torr Pressure

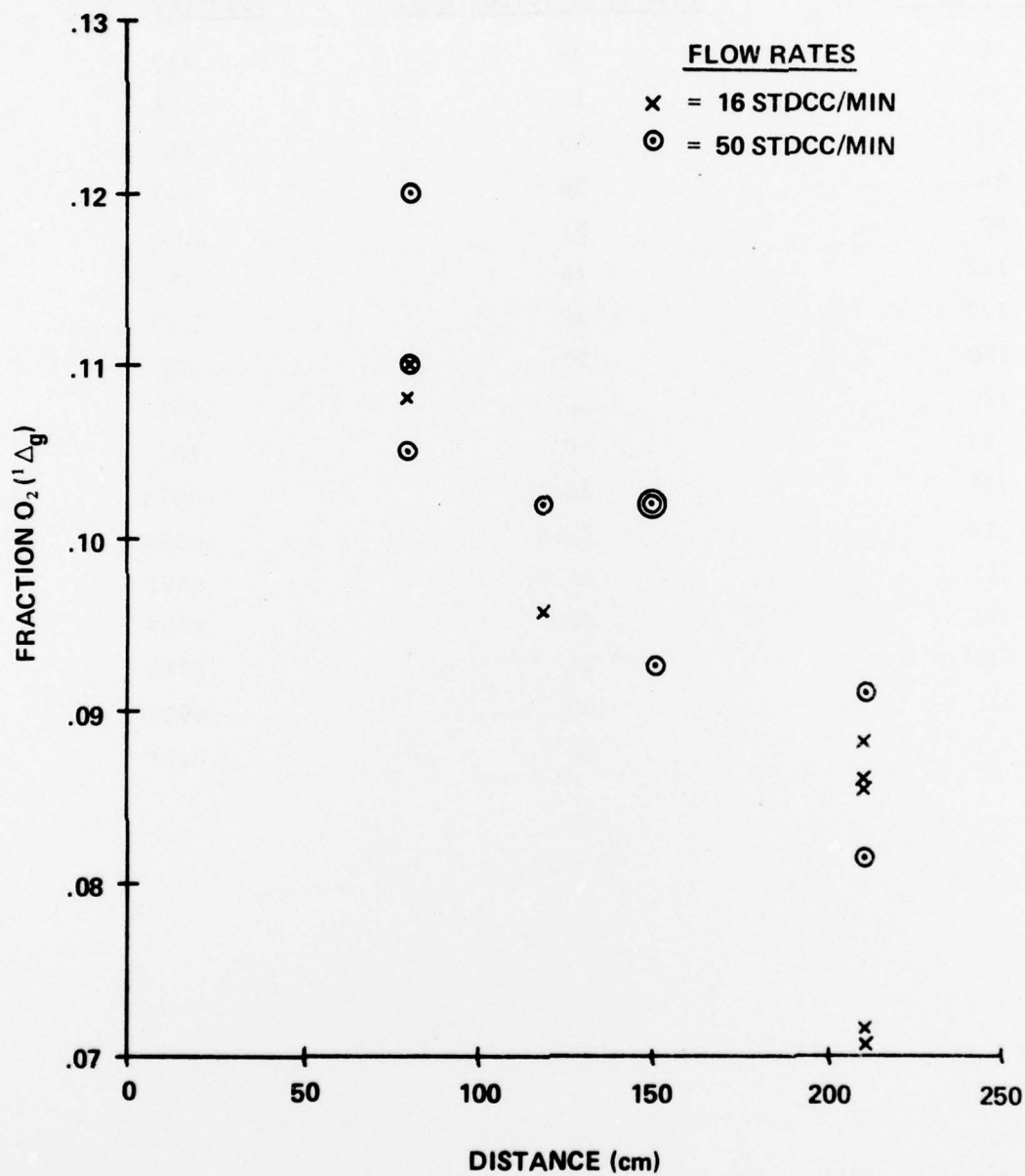| Distance (cm)	Flow Rate (STDCC/min)	Fraction ($^1\Delta_g$)
80	16	.110
80	16	.108
80	50	.110
80	50	.120
80	51	.105
122	16	.0958
122	50	.102
150	50	.102
150	50	.0926
150	50	.102
211	15.5	.0853
211	15.5	.0859
211	15.5	.0881
211	16	.0707
211	16	.0715
211	50	.0909
211	50	.0814

FIGURE 4. FRACTION OF $O_2('\Delta_g)$ AS A FUNCTION
OF DOWNSTREAM DISTANCE AT 1.00 TORR.

12

The data shows that self- and/or wall deactivation of $O_2(^1\Delta_g)$ under these conditions can be substantial over a few hundred centimeters of flow distance. No attempt was made to separate the wall from the self-deactivation or to calculate a rate constant for the deactivation.

The pressure of the system was varied from .5 to 2.0 torr. There is an obvious dropoff in $O_2(^1\Delta_g)$ production at pressures above 1.5 torr. Below 1.5 torr, there seems to be only a small increase in $O_2(^1\Delta_g)$ production as the pressure is decreased.

Deactivation of $O_2(^1\Delta_g)$ by Cl_2
_____

Two sets of experiments were run. In the first, the total distance from the microwave cavity to the ESR was 75 cm. The Cl_2 or Ar injection port was 20 cm downstream from the microwave unit. The O_2 pressure alone was 1.11 torr, with the total pressure being 1.33 torr. With Ar as the deactivant, the average fraction of $O_2(^1\Delta_g)$ over six measurements was .116 ± .011. The average over six runs with Cl_2 as the deactivant was .115 ± .011. Thus there appears to be no deactivation over and above that caused by Ar.

In the second set of experiments, the deactivant injection port was moved to a distance of 155 cm to give time for more deactivation. Under these same pressure conditions stated above, the Ar-deactivated fraction of $O_2(^1\Delta_g)$ was .062, while the Cl_2-deactivated fraction was .077. These values are based on only two measurements each, so their accuracy is questionable. Once again, however, Cl_2 certainly appears to no more effectively deactivate $O_2(^1\Delta_g)$ than Ar. When the total system pressure was raised to 1.9 torr, the Cl_2-deactivated fraction was .057 while the Ar-deactivated fraction was .067, this time based on only one data point each.

Based on the results of the first set of experimental conditions an estimate of the upper limit of the deactivation rate constant of Cl_2 on $O_2(^1\Delta_g)$ has been made. It was estimated that, at most, the Cl_2 deactivated the $O_2(^1\Delta_g)$ by 10% more than the Ar. Based on this, a second order deactivation of $O_2(^1\Delta_g)$ by Cl_2, the Cl_2 pressure, and the

14

distance and flow rate, an upper limit for the second order rate constant of 10^{-16} CC/moles-sec has been estimated.

The fact that no deactivation could be conclusively shown with Cl_2 underscores the need for more accurate measurements. These measurements are planned for the near future.

Determination of HCl Content from a Chemical Generator

The reaction of Cl_2 with the basic hydrogen peroxide clearly produced the $O_2(^1\Delta_g)$ as determined by the red glow of the $[O_2(^1\Delta_g)]_2$ dimol radiation above the solution. The gaseous products trapped were inserted into the mass spectrometer. No other species except an apparent increase in the O_2 peaks over that of the background air spectrum appeared. However, insertion of pure Cl_2 into the mass spectrometer showed that very high pressures of Cl_2 (on the order of atmospheric pressure) were needed before any chlorine species could be observed. Furthermore, the Cl_2 was apparently reacted in the mass spectrometer with contaminants such as H_2O vapor to produce HCl. Therefore, it appears any Cl_2 in the reactor effluent may show up as HCl on the mass spectrometer. Further research into the possibility of detecting HCl with this instrument, including contact with the manufacturer, produced discouraging forecasts[7].

Infrared spectrometry was selected as a possible alternative for observing HCl. Experiments with gas samples of HCl showed that the instrument lacked sensitivity to detect HCl partial pressures in the range of those present in the chemical generator system. However, it was sensitive enough to detect HCl in the 10-20 torr pressure range. Freezing out of the reaction gaseous products with LN_2 and subsequent

15

introduction into the IR cell could allow enough HCl to be detected in the gas phase. This approach will be attempted in the near future.

IV. CONCLUSIONS AND RECOMMENDATIONS

The maximum $O_2(^1\Delta_g)$ fraction which can be produced from one microwave cavity is about .125 at 1 torr O_2 pressure. Self-deactivation and wall deactivation can be substantial over several hundred centimeters of tubing.

Deactivation of $O_2(^1\Delta_g)$ by Cl_2 appears to be of the same order of magnitude as that of Ar. More detailed experiments are needed to obtain a quantitative rate constant. Measurements of the deactivation of I* by Cl_2 are also needed.

Infrared spectrometry appears to be feasible in the determination of whether appreciable HCl is produced with the Cl_2/H_2O_2 chemical generator. Mass spectrometry with our current system seems to be fraught with insurmountable problems in this determination.

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